Chemical Leaching Near the Waiawa Shaft, Oahu, Hawaii: 1. Field Experiments and Laboratory Analysis

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Abstract

This paper is the first paper of a two-part series concerned with assessing the potential for organic chemical leaching to a ground-water skimming tunnel in the Pearl Harbor Basin, Oahu, Hawaii as a direct result of a proposed urban development. The objective of our simulation-based assessment was to provide insight into the potential for chemicals, that may be introduced to the recharge areas of the Waiawa Shaft as a result of the proposed developments, to subsequently leach through the unsaturated zone to ground water. In this paper field and laboratory results are presented for experiments designed to support the modeling effort reported in the second paper of this series. The chemical leaching experiments were conducted at two field locations. The chemicals which were applied and then monitored for their downward movement in the near-surface unsaturated zone are bromide, chlorpyrifos and fenamiphos. We found (1) good mass balance for bromide at both sites, (2) limited mobility of chlorpyrifos and fenamiphos at the field plots, and (3) good agreement between field and laboratory measured degradation rates.

Introduction

The fate of organic chemicals applied at or near the surface, relative to the contamination of underlying ground-water resources, is of great concern. Several elaborate studies have been undertaken to characterize the movement of pesticides and other organic chemicals in the vadose zone (e.g., Jury et al., 1982). Often, however, leaching experiments are not designed with a subsequent and specific modeling application in mind. In this paper we describe a set of experiments carried out to calibrate the EPA's Pesticide Root Zone Model (PRZM) (Carsel et al., 1984) for the purpose of making long-term estimates of vertical chemical movement in proposed development areas. The PRZM simulations are reported in the companion paper (Loague et al., 1994).

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The recognition of potential sources of ground-water contamination in Hawaii, as elsewhere, is of great environmental concern. In Hawaii this is especially true as more than 90% of the population depends upon ground water for their domestic supply. The Hawaii State Department of Health has released maps which summarize the types and quantities of chemicals which have been confirmed in Hawaiian ground water (Au, 1991). The detected levels of chemicals in Hawaii's ground water may not pose a health risk, but they do demonstrate the vulnerability of this precious resource. On Oahu, where approximately 80% of Hawaii's million-plus population resides, known resources are almost totally exploited; therefore, prevention of further contamination through enlightened management is essential.

Proposed urban developments by the Gentry Company on Waiawa Ridge and the U.S. Navy in the Waiawa Valley pose a possible threat to the Navy's domestic water supply. Waiawa is located in the central area of the Hawaiian island of Oahu (Figure 1) and overlies a section of the Pearl Harbor aquifer, which is recognized as one of the most important sources of potable water in the state. The Navy's Waiawa Shaft operates as an unlined basal ground-water skimming tunnel which extracts approximately 60,000 m^3/day from the Pearl Harbor aquifer. The urban developments are expected to lie directly above and adjacent to the Waiawa Shaft. The urban developments could potentially result in a wide range of chemicals being introduced at the ground surface, including: (1) termiticides for housing developments, and (2) fertilizers and pesticides for golf courses and residential area applications. These chemicals may contaminate the water extracted from Waiawa Shaft by leaching from the ground surface, through the unsaturated zone, and into ground water.

The Navy contracted the University of Hawaii Water Resources Research Center (UHWRRC) to assess the potential for ground-water contamination at the Waiawa Shaft due to expected chemical applications at the proposed development sites. The UHWRRC assessment (Oki et al., 1990) is based upon estimates of pesticide and fertilizer use, ground-water recharge, and chemical transport through the unsaturated and saturated zones.

The proposed urban development in the vicinity of the Waiawa Shaft provides an opportunity to question what potential impacts may result from the land-use changes before the changes are made. The question of chemical use in the development area is not an academic one. The Formosan subterranean termite is a major problem in Hawaii, and application of a chemical drench is the established method of control. A suite of fertilizers and pesticides are routinely employed in residential areas and at golf courses to maintain gardens and turf. A survey of chemical use in existing residential areas near the proposed development area was conducted for this study to identify chemicals that might be potential contaminants of the Waiawa Shaft as a result of development. The results of the survey are presented by Oki et al. (1990). The chemicals in the leaching experiments reported here and those used in the long-term simulations were selected for their likely importance if development is allowed to proceed. Chemicals included in the field experiments for model calibration represent a broad spectrum of chemicals in terms of mobility and persistence.

Waiawa Shaft, Oahu, Hawaii

The history of contamination at Waiawa Shaft illustrates the vulnerability of the resource. During the early 1960s the chloride concentration of water from the Waiawa

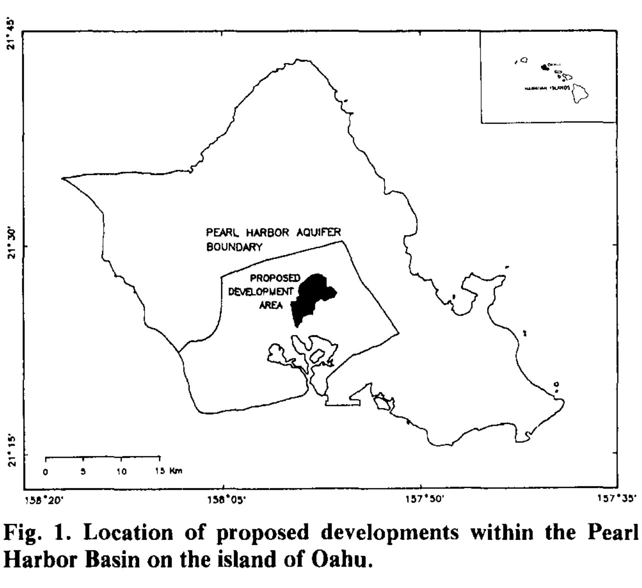

Fig. 1. Location of proposed developments within the Pearl Harbor Basin on the island of Oahu.

Shaft was typically about 100 mg/l. Chloride concentrations rose during the 1970s until, in 1979, the levels approached 300 mg/l. The cause of this chloride contamination was postulated (Eyre, 1983) to be the irrigation of sugar cane on Waiawa Ridge with water having chloride concentrations exceeding 1,000 mg/l. Furrow irrigation methods enhanced the downward movement of water and chloride through the unsaturated zone causing contamination of the basal water. Sugar cane has not been cultivated in the Waiawa Ridge area since 1983; consequently, the chloride levels in water pumped from the Waiawa Shaft have dropped significantly, and are currently about 50 mg/l (Public Works Center, 1989).

Trace levels of 1,2-dibromo-3-chloropropane (DBCP), 20 parts per trillion (PPT) or less, and 1,2,3-trichloropropane (TCP), less than 200 PPT, were detected in the Waiawa Shaft in 1983. Upgradient pineapple fields are the suspected source of this contamination (Oki and Giambelluca, 1987). The history of contamination at Waiawa Shaft illustrates the vulnerability of the resource.

Objectives

The primary objective of this effort was to estimate the amounts of selected chemicals, originating from the proposed Waiawa developments, which may leach through the unsaturated zone and into ground water. In this study, long-term simulations, in conjunction with field leaching experiments, were used to provide an assessment of the potential for ground-water contamination by chemicals likely to be applied as a result of the proposed developments. The scope of the effort reported in this paper and the companion paper (Loague et al., 1994), with respect to the UHWRRC project, is shown by the shaded portions of Figure 2.

Description of Development Sites

Waiawa Ridge

The proposed Waiawa Ridge community would include single family units, low- and medium-density apartments, retail commercial spaces, mixed commercial and industrial areas, school and park areas, golf courses, and a botanical garden over an area of about 1000 ha. Ground elevations range from about 50 to 300 m above sea level. The Waiawa infiltration tunnel runs beneath the eastern edge of Waiawa Ridge where the ground surface is at an elevation of about 120 m. Currently the land on Waiawa Ridge is used primarily for cattle grazing.

Climate and Soils. The average annual rainfall on Waiawa Ridge varies from less than 1 m near the southwest extent to about 2.5 m at the northeast end of the development near the higher elevations of the Koolau Range. The corresponding annual pan evaporation rates are about 2 m at the lower southwest extent and 1 m at the higher elevations. The Molakai, Lahaina, and Waiawa soil series, all from the Oxisols order, are the most common soil types mapped on the Waiawa Ridge (Foote et al., 1972).

Geology and Hydrogeology. The proposed Waiawa Ridge development is located on land built by successive

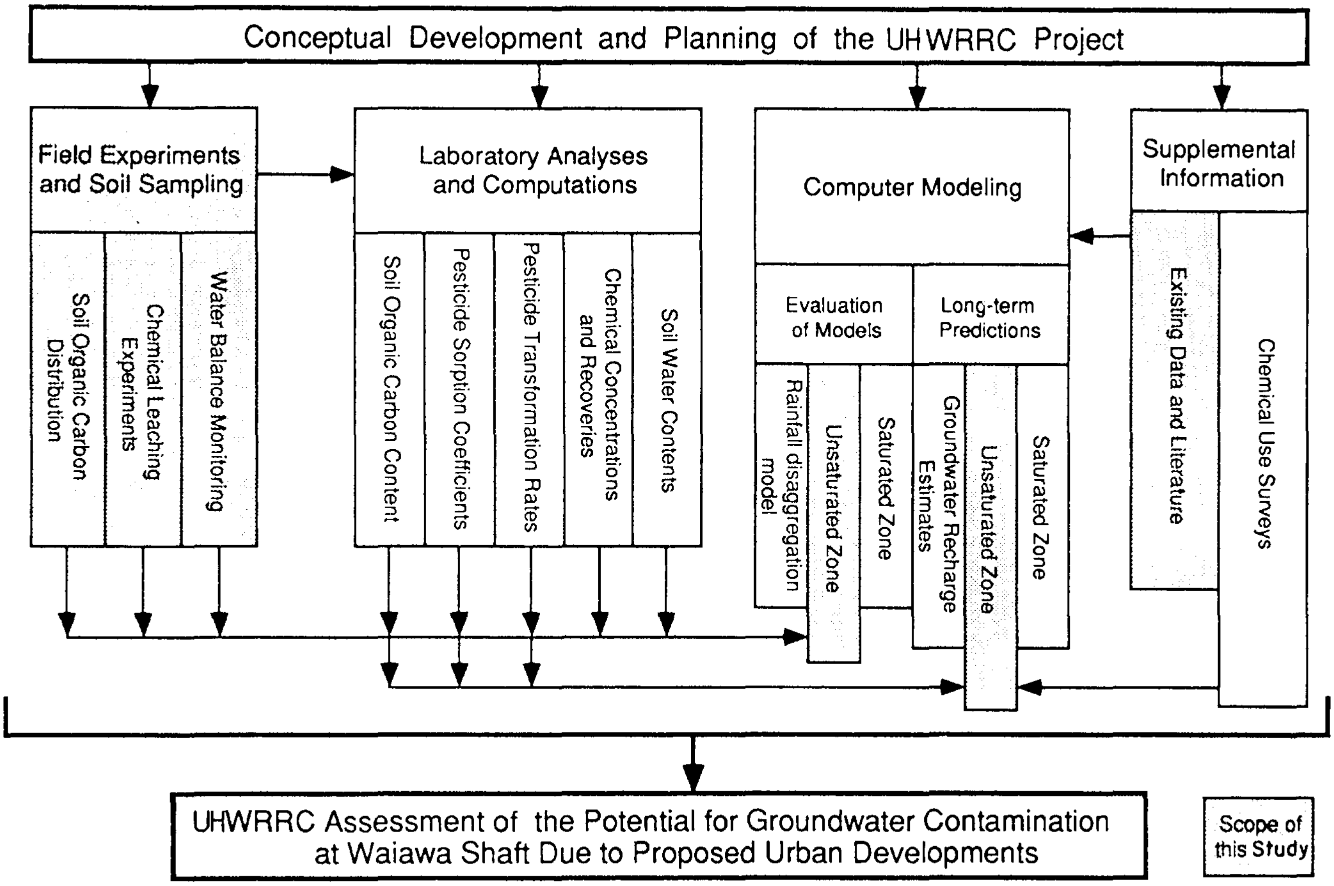

Fig. 2. Scope of this study relative to the entire University of Hawaii Water Resource Research Center (UHWRRC) project.

lava flows of the Koolau shield volcano. The thin basaltic lava flows of pahoehoe and ‘a‘a, usually less than 3 m thick, which make up the Koolau Basalt are very permeable and typical of Hawaiian shield volcanoes. The relatively unweathered basalt at depth grades into highly weathered basalt, commonly called saprolite, as it approaches the surface. Saprolite then grades into soil near the ground surface. The depth to the boundary between the basalt and saprolite of Waiawa Ridge is approximately 25 m but can be as shallow as 10 m (Public Works Center, 1951). Depth to the basal water table is about 45 m near the southern tip of the development and over 300 m at the northern boundary of the development. The saturated hydraulic conductivity of the basalt has been estimated at approximately 400 m/day; the natural hydraulic gradient is approximately 0.0002 (Mink and Lau, 1980).

Waiawa Valley

The proposed Navy development in Waiawa Valley consists of 114 housing units over an area of less than 30 ha. Ground elevations in the Waiawa Valley development are between 30 and 50 m above sea level. Prior to its use as an aviation supply depot in World War II by the Navy, the development site in the Valley was cultivated with pineapple and vegetable crops. Currently, the area is overgrown with guinea grass and koa haole.

Climate and Soils. Average annual rainfall at the Navy site in Waiawa Valley is approximately 1 m with a pan evaporation rate of about 2 m. The valley floor consists primarily of flatter alluvial terraces grading into moderately sloping, rocky talus material at the base of the gulch wall. The Kawaihapai soil series of the Mollisol order is the most common soil type mapped within the Waiawa valley (Foote et al., 1972).

Geology and Hydrogeology. Beneath Waiawa Stream, which runs through the proposed Navy development site, lies a thick layer of alluvium. Beneath the alluvium, heavily weathered basalt grades into fresh unweathered rock. Due to the presence of saturated sediments above the basalt, weathering of the underlying rock has been very effective, extending to depths greater than 60 m below the alluvium. Injection well tests conducted in a Waiawa Valley borehole on a 48 m thick column of weathered rock yielded an average hydraulic conductivity of 0.018 m/day (R.M. Towill Corp., 1978). Exploratory wells drilled near Waiawa Stream (Public Works Center, 1951) reveal a water table about 15 m below the ground surface. Within the proposed Navy development this corresponds to an alluvial aquifer water-table elevation of about 30 m above sea level. This is considerably higher than the basal water table which is at an elevation of about 6 m. The exact hydraulic relationship between the alluvial aquifer and the Waiawa Shaft or the basal ground water is unknown.

Field Experiments

Two field plots were established for the application of chemicals and subsequent monitoring of downward leaching through the soil profile. Criteria for selecting the locations of the field plots were: (1) locations within the proposed development sites; (2) relatively homogeneous soil properties laterally within each plot to isolate the temporal chemical leaching effects; (3) level topography to minimize the potential for surface runoff and erosion; (4) easy access to minimize efforts in plot preparation, monitoring, and maintenance. Due to problems encountered in obtaining access to key locations on Waiawa Ridge (perceived liability) and constraints in resources, tests were established at only two plot locations; the first was located in Waiawa Valley and the second at University of Hawaii Poamoho Research Station (UHPRS). The Waiawa soil on the Poamoho site is the same soil series as one of the three major soil series on Waiawa Ridge. Each experimental site had an area of 0.011 ha.

Trenches, approximately 0.15 m deep and 0.4 m wide, were dug around the perimeter of each plot to prevent surface runoff and erosion from surrounding areas from entering the plots. Using soil from the trenches, berms were built between the trenches and plot boundaries to ensure that runoff and erosion from within the plot remained within its boundaries. Both of the field sites were divided into quadrants (plots) of equal area; three of the quadrants were used to measure leaching while the fourth was used for infiltration tests and the determination of soil-water contents.

The Waiawa Valley test plot site was located within the proposed Navy development area, at an elevation of approximately 45 m above sea level on one of the more permeable soils found in the Waiawa Valley. Existing vegetation was cleared from an area extending at least 5 m beyond the plot boundaries; the vegetation was cut down to the soil surface with little disturbance of the soil. The Poamoho test plot site, at an elevation of approximately 215 m, was first cleared of a corn crop residue and then tilled to loosen the soil. The area was then raked to level the gently sloping topography. The geology and hydrogeology of the Poamoho test plot site is quite similar to that of Waiawa Ridge. Since the chemical leaching experiments performed on the Poamoho test plot involved, at most, the top three meters, properties of the profile below this depth were not relevant to this study. Vegetation cover at both sites was minimal at the time of the first chemical applications and was kept at a relatively short and uniform length thereafter. A portable irrigation system was used to induce chemical leaching at both test plots. Average annual rainfall at the Poamoho test plot site is 1 m with an average pan evaporation rate of about 2 m. In terms of elevation and climate, the Poamoho test plot site is representative of mid-elevations on Waiawa Ridge. At each plot laboratory analyses for soil organic carbon content, soil bulk density, soil-water content, chemical concentrations, sorption coefficients, and transformation rates were conducted. The data obtained from the two experimental sites were used to calibrate PRZM (Loague et al., 1994).

Chemical Leaching

The chemicals applied to the field plots were: bromide (as NaBr); chlorpyrifos (trade name Dursban), an organophosphate termiticide; and fenamiphos (trade name Nemacur), an organophosphate nematicide. Bromide served as a conservative tracer while the two pesticides provided a relatively wide range in sorption and degradation properties to evaluate PRZM (Loague et al., 1994). The fenamiphos metabolite, fenamiphos sulfoxide, is a relatively mobile and persistent chemical, while chlorpyrifos is very strongly sorbed and is less persistent in soil. Fenamiphos was also selected because of its prior study in Hawaiian soils (Lee et al., 1986; Lee, 1987; Schneider et al., 1990) and its widespread use in pineapple. Chlorpyrifos is one of the most popular termiticides used by local pest control operators in Hawaii.

Each of the quadrants set aside for leaching experiments at the two test plots received 0.164 kg of NaBr, 0.114 liters of Dursban 2E, and 0.027 liters of Nemacur 3E which were mixed into 7.6 liters of water and evenly applied to the soil surface with a backpack sprayer with two nozzles spaced 0.51 m apart. (Note: the first application at the Waiawa test plot received only half as much NaBr). The respective application rates for bromide and the active ingredients chlorpyrifos and fenamiphos were 45.7, 9.8, and 3.48 kg/ha. To insure chemical incorporation into the soil, the test plots were preirrigated, then irrigated again with 12 mm of water immediately following the application. A second chemical application to the Waiawa plot was performed six months after the initial application, when the pesticide concentrations from the first application had diminished below the detection limit.

Prior to chemical applications, soil samples were collected at various depths from the perimeter of the field plots to determine the background concentrations of the three chemicals that were applied. The soil samples used for chemical analyses were collected on several occasions after the applications to define the temporal characteristics of the leaching process. To obtain better representations of the concentration profiles, samples were obtained at two locations in each of the three quadrants which received chemicals. On each sampling date, the six sampled profiles were collected.

Soil profiles for pesticide analyses were collected in duplicate from each of the three treated plots at each site. At Waiawa, soil residue samples were collected 4, 38, and 124 days after the first pesticide application, and 17 and 122 days after the second pesticide application. At the Poamoho site, soil residue profiles were collected 11, 53, and 100 days after pesticide application. Soil profiles were collected using bucket augers using a methodology similar to that described by Schneider et al. (1990). Auger samples were collected at 0.1 m intervals to a depth of 0.3 m; the sampling interval was then increased to 0.15 m below 0.3 m. Exceptions to this procedure occurred during the initial samplings after applications, when 0.05 m deep samples were collected at the soil surface to provide improved resolution of the concentration profiles. The sampling depth was increased with each sampling time.

Soil Organic Carbon

Four soil transects were established to determine the spatial variability of soil organic carbon, the primary soil property affecting sorption of organic pesticides. Three straight-line transects aligned with the prevailing slope were established on Waiawa Ridge. Each of these transects were located within one of the three dominant soil series: Molokai, Lahaina, and Waiawa. The fourth transect, which includes a two-dimensional grid, was located in Waiawa Valley within the Kawaihapai soil series. Soils from the transects were collected at the surface and at 0.3 m depth intervals to a depth of 1.2 m.

Water Balance Estimates

Rainfall at the Waiawa test plot site was digitally recorded on an hourly basis and summed to provide daily values. There were several gaps in the rainfall record due to data logger malfunctions, which were filled using data from a manually read back-up gage installed at the plot. When necessary, the back-up data were disaggregated to a daily basis by comparison with U.S. National Weather Service data from a gage in the nearby Pacific Palisades area. Rainfall at the Poamoho test plot site was recorded daily by UHPRS personnel at a weather station located about 100 m from the test plot. The back-up gage installed at the Poamoho test plot site was not needed as there were no gaps in the UHPRS rainfall data.

Potential evapotranspiration at the Waiawa test plot site was estimated by the Priestley-Taylor (1972) method using net radiation data recorded at the plot. Data gaps in the net radiation were either interpolated or filled using monthly average values. At the Poamoho test plot site a standard Class A evaporation pan was installed beside the UHPRS weather station, which also houses a solar radiometer and an additional evaporimeter. There was a total of 15 days of missing information at the Poamoho test plot site; these gaps were filled in by assuming a pan evaporation rate of 1.78 m per year (from Ekern and Chang, 1985). The annual pan evaporation rate was disaggregated into monthly values by using historical data from the two nearest stations; these stations have six years of continuous data between them (Ekern and Chang, 1985). The two historical data sets were normalized and averaged to obtain the monthly variation. Pan evaporation for the missing periods was equally distributed to accommodate PRZM's daily time step. These daily pan values were used with a pan factor of 0.33 (Ekern, 1966) to estimate potential evapotranspiration for the Poamoho test plot site. The pan factor of 0.33 corresponds to a bare soil in Hawaii, thus approximating the sparse vegetative cover at the Poamoho test plot site.

Laboratory Analyses

Chemical Analyses

Pesticide Residue Analysis

Soil samples were passed through a 4-mm sieve to homogenize the sample prior to pesticide extraction. Subsamples (50 g) were extracted in ethyl acetate using a wrist-action shaker (Schneider et al., 1990). Soil extracts were then analyzed for chlorpyrifos, fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone by gas chromatography using a Hewlett Packard 5890A-GC with a nitrogen-phosphorus detector (NPD) and HP 7673A autosampler using the method of Crepeau et al. (1991). The lower detection limit for each compound was 7 $\mu g/kg$ of soil on a dry soil basis. Soil samples from each field site were fortified with 1 ml of a mixture of chlorpyrifos and fenamiphos at a concentration of 5 mg/l and extracted 24 hours after fortification. For the Waiawa soil, the average recoveries were 85% (± 5.3%), and 92.1% (± 4%), for chlorpyrifos and total fenamiphos, respectively. The average recoveries for the Poamoho soil were 86.5% (± 4%), and 96.1% (± 5.2%) for chlorpyrifos and fenamiphos, respectively.

Bromide Analysis

Soils were subsampled (50 g aliquots) for bromide analysis and extracted with distilled water using a soil:water ratio of 1:1. Soil-water suspensions were agitated on an orbital shaker for one hour at 350 RPM. Samples were centrifuged and the supernatant was collected for analysis using an Orion (Model 94-35) Bromide ion selective electrode (Adriano and Donner, 1982). To test the extraction efficiency of the method, soil samples from each field site were equilibrated with two bromide solution concentrations, 3.4 and 11 mg/l (1:1 solution soil ratio, 50 ml:50 g of soil) for one hour. The bromide recovery for the 3:4 mg/l concentration averaged 111% (± 7%) for both Waiawa and Poamoho soils. At a concentration of 11 mg/l, the average recovery was 109% (± 4%) for Waiawa soil and 122% (± 3%) for the Poamoho soil. The bromide concentrations in the soil profiles were corrected for background levels of 0.5 mg/kg and 0.2 mg/kg at the Waiawa and Poamoho test plots, respectively.

Chemical Sorption and Transformation

Laboratory Sorption Measurements

In order to derive site-specific sorption coefficients, K_d and K_{oc}, representative soils were collected from the two experimental sites, Waiawa Valley and Poamoho Experiment Station, and from the three soil series (Lahaina, Molokai, Wahiawa) present on Waiawa Ridge. Sorption isotherms were determined for the field plot soils over a range of concentrations. Untreated soils from the field plots were collected from two locations and two depths, 0-0.2 m, and 0.35-0.55 m. Sorption isotherms were determined using the batch sorption method (Lee, 1987; Green et al., 1993). ^{14}C labelled chlorpyrifos (DowElanco, Inc.) and ^{14}C labelled fenamiphos sulfoxide (Miles, Inc.) were used in the experiments. Three concentrations of chlorpyrifos (0.18, 1.0, 2.5 mg/l) and four levels of fenamiphos sulfoxide (0.15, 0.45, 3.3, 6.5 mg/l) were used. Soils were equilibrated in duplicate with pesticide solutions at ambient laboratory temperature (22 ± 2° C) with a solution/soil ratio of 5:1, over an equilibration period of four hours for chlorpyrifos and 24 hours for fenamiphos sulfoxide.

K_{oc} values were determined for the Waiawa Ridge samples at a single pesticide concentration (1.0 mg/l). Soil samples were collected from each of the three soil series from two locations and two depths (0-0.2 m, 0.65-0.9 m).

Laboratory Degradation Measurements

Pesticide degradation measurements were conducted as described by Lee (1987). Untreated soils from three sites and two depths were collected from the Waiawa and Poamoho field plots. The Waiawa Ridge soils were those used for the sorption study. Degradation experiments were initiated within two weeks of sample collection. Soils (16 g) were treated with a mixture of chlorpyrifos and fenamiphos sulfoxide at a ratio of 5 $\mu g/g$ of soil, and incubated in duplicate at 30° C under aerobic conditions for one month. The soil-water content was adjusted 33 kPa tension prior to the experiment. Samples were extracted and analyzed by gas chromatography (as described previously) at four time intervals: 0, 3, 14, and 28 days after the start of the experiment. The Waiawa plot degradation experiment used fenamiphos (parent) instead of fenamiphos sulfoxide.

Soil-Water Content, Bulk Density, and Soil Organic Carbon

Gravimetric soil-water contents were determined for field samples by oven drying at 105° C for 24 hours. Soil bulk density was determined using the core method as described by Blake and Hartge (1986). Once bulk density was known, the volumetric water content was estimated by $\theta = \theta_g \rho_b / \rho_m$, where θ is the volumetric soil-water content (m^3/m^3), θ_g is gravimetric soil-water content (kg/kg), ρ_b is soil bulk density (kg/m^3), and ρ_m is the soil-water density (kg/m^3); ρ_m is assumed to be 1000 kg/m^3. Soil samples from the two field sites and the four transects were oven-dried and powderized prior to measuring their organic carbon contents with a Leco WR-112 Carbon Determinator.

Field and Laboratory Results
Chemical Leaching Experiments

The Waiawa plot was irrigated on several occasions during the summer months to supplement the lower rainfall and to induce leaching. The low water input to the unirrigated Poamoho site is reflected by the very low simulated recharge. Although surface runoff was always assumed to be zero, there was an undetermined amount of runoff at the Poamoho test plot site in early March as evidenced by a breach in one of the berms. The chemical application and sampling events are superimposed in Figure 3 with water inputs for the two test plots. Daily meteorologic files from both test plot sites which were input to PRZM (Loague et al., 1994) are reported by Miyahira (1990).

The bromide concentration data from each of the six sampled holes collected on each of the eight collection dates are reported by Miyahira (1990). Bromide concentration profiles which summarize these data are illustrated in Figure 4. Bromide concentration profiles for the Waiawa site show an average coefficient of variation (CV) of 0.36 between soil profiles within each quadrant and a CV of 0.47 between plots. Similarly, the CV's for the Poamoho site were 0.30

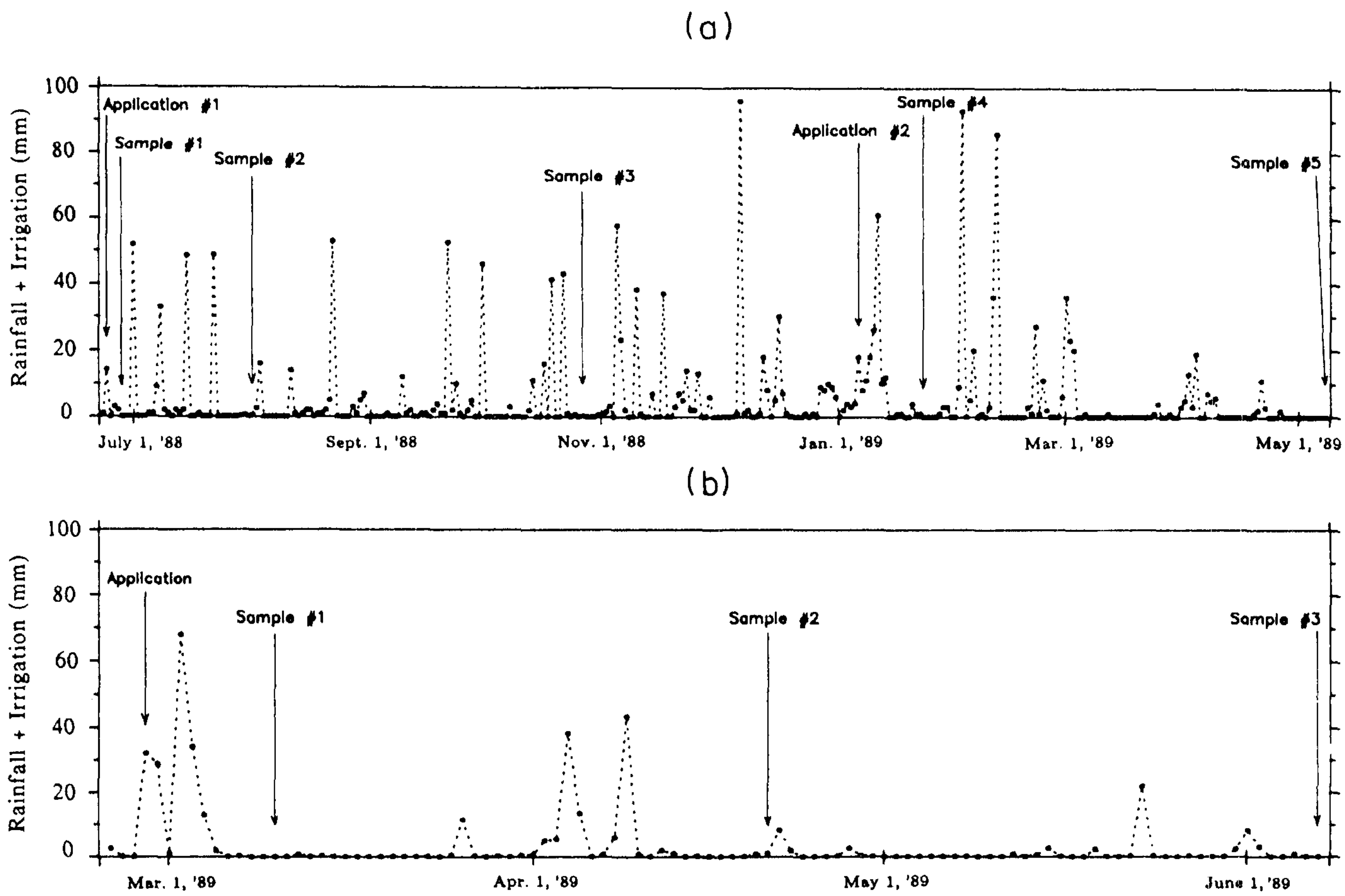

Fig. 3. Time-series of events of field sites. (a) Waiawa, 318 days. (b) Poamoho, 100 days. Application #1 denotes first chemical application.

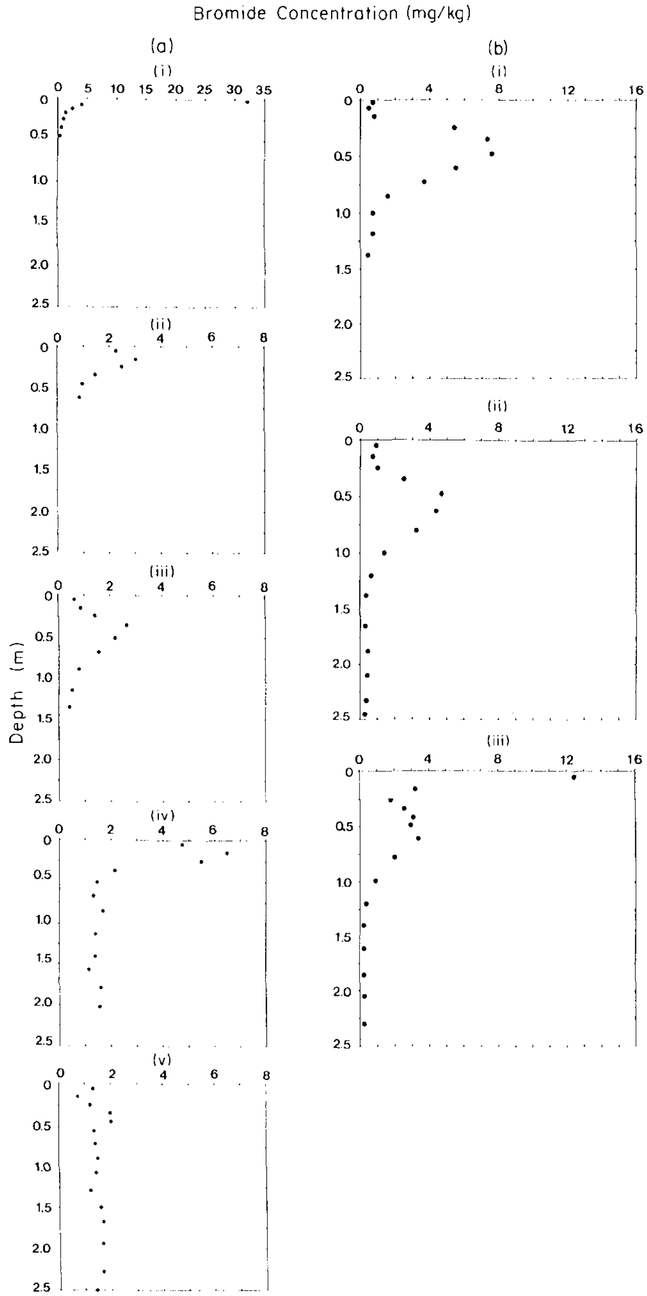

Fig. 4. Observed bromide concentration profiles (note changes in axis scales). (a) Waiawa site at five times: (i) 4 days after first application; (ii) 38 days after first application; (iii) 124 days after first application; (iv) 213 days after first application, 17 days after second application; (v) 318 days after first application, 122 days after second application. (b) Poamoho site at three times: (i) 11 days after application; (ii) 53 days after application; (iii) 100 days after application.

and 0.42 for within and between plots, respectively. The mass balance of bromide at both the Waiawa and Poamoho test plot sites (see Table 1) reveals good recoveries for the amount applied for each of the five sampling dates, with an increase in lost mass with time. A complication is observed during the third sampling at the Poamoho test plot site where bromide moved upward; this was apparently caused by a capillary transport mechanism as the soil became very dry between the second and third sampling dates.

Table 1. Mass Balance for Bromide at the Waiawa and Poamoho Test Plots

Sample date	*Waiawa Plot*			*Poamoho Plot*		
	Mean	*SD**	*Range*	*Mean*	*SD**	*Range*
1	0.97	0.25	0.65-1.26	1.03	0.35	0.73-1.67
2	0.43	0.19	0.17-0.66	0.78	0.53	0.22-1.43
3	0.53	0.20	0.24-0.86	0.83	0.32	0.52-1.29
4	0.76	0.35	0.19-1.21			
5	0.54	0.28	0.19-0.89			

*SD = standard deviation.
Mass balance recoveries expressed as a fraction of the amount applied. Means are based on 6 soil profiles. Waiawa sample dates correspond to 4, 38, 124 days after the first chemical application; and 17 and 122 days after the second application. Poamoho sample dates correspond to 11, 53, and 100 days after application.

The pesticide concentration data for chlorpyrifos and fenamiphos are tabulated by Miyahira (1990). The concentrations of fenamiphos measured from the field plots are presented as total of fenamiphos, which includes the parent compound, fenamiphos, and its metabolites, fenamiphos sulfoxide and fenamiphos sulfone. Concentration profiles which summarize the movement of chlorpyrifos and fenamiphos are illustrated in Figures 5 and 6. These data are not corrected for extraction recoveries. The amount of chlorpyrifos leaching below 0.5 m was negligible at both plots, with the great majority of mass remaining within the top 0.2 m for all sampling dates. Fenamiphos showed greater variability than chlorpyrifos in its concentration profiles and was even less persistent. Fenamiphos also showed minimal leaching, although the first sampling at Poamoho showed detectable levels down to about 0.7 m. In either case, both chlorpyrifos and fenamiphos behaved as relatively immobile and nonpersistent pesticides. Mass balances of the pesticides were used to calculate their degradation rates in the field. These results reveal that unless disproportionate amounts of pesticide masses were lost just after applications (i.e., preferential flow or lateral dispersion), the degradation rate coefficients decrease with time and therefore do not follow the assumed first-order kinetics.

Pesticide Transformation and Sorption

Summaries of laboratory measured transformation and sorption characteristics for chlorpyrifos and fenamiphos sulfoxide are shown in Tables 2 and 3, respectively. Chlorpyrifos is transformed in soil by chemical hydrolysis to the metabolite 3,5,6-trichloro-2-pyridonol (Racke and Robbins, 1991). The oxidation of fenamiphos in soil to the metabolites fenamiphos sulfoxide and fenamiphos sulfone is thought to be meditated by soil microbial activity (Ou and Rao, 1986). Field dissipation rates (Miyahira, 1990) reveal that chlorpyrifos was more persistent than total fenamiphos for both Waiawa and Poamoho field plots. They also indicate that chlorpyrifos was more persistent than in the laboratory incubations and more persistent at the Waiawa test plot compared with the Poamoho plot. Field and laboratory transformation rates were comparable for total fenamiphos. Calculated field dissipation rates show a greater persistence of total fenamiphos at Poamoho compared with Waiawa, with first-order rate coefficients of 0.026 and 0.052 day^{-1}, respectively (Miyahira, 1990). The laboratory measured transformation rates for chlorpyrifos, corresponding to half-lives of 7-14 days, fall within the range of published data (Racke, 1993). The values reported here for fenamiphos degradation are also in agreement with literature values (Wauchope et al., 1992).

Measured sorption values of chlorpyrifos on soils from the Poamoho and Waiawa test plots fall near the lower end of the range of K_{OC} values reported in the literature (0.973-31.0 m^3/kg) (Racke, 1993). The chlorpyrifos K_{OC} values reported here are in agreement with other values reported for Hawaii soils (Green et al., 1993).

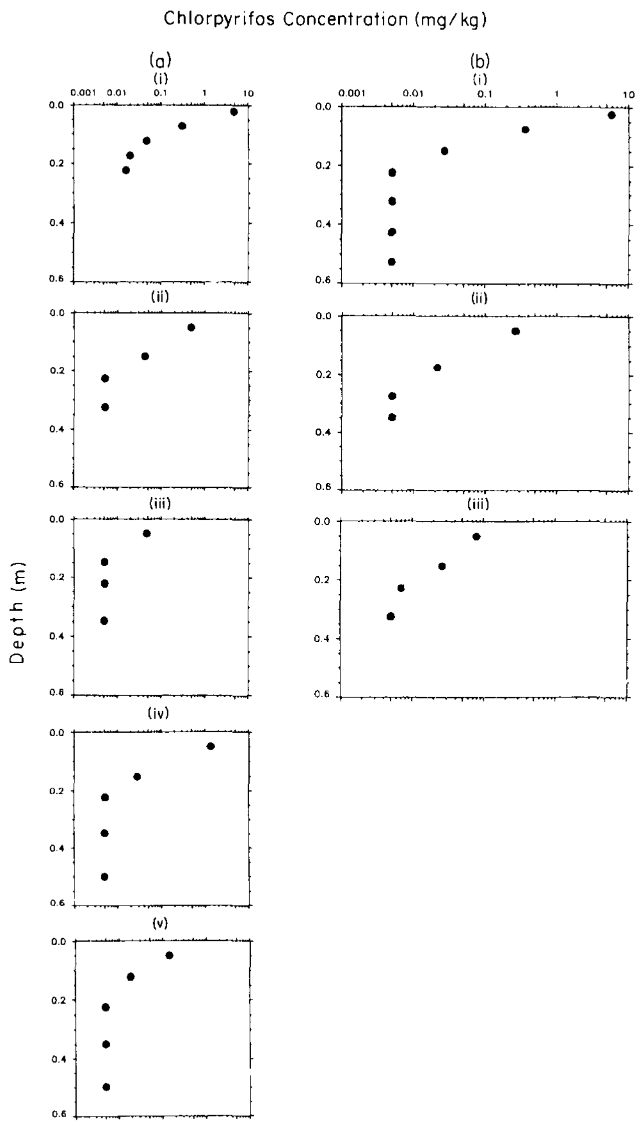

Fig. 5. Observed chlorpyrifos concentration profiles. (a) Waiawa site at five times: (i) 4 days after first application; (ii) 38 days after first application; (iii) 124 days after first application; (iv) 213 days after first application, 17 days after second application; (v) 318 days after first application, 122 days after second application. (b) Poamoho site at three times: (i) 11 days after application; (ii) 53 days after application; (iii) 100 days after application.

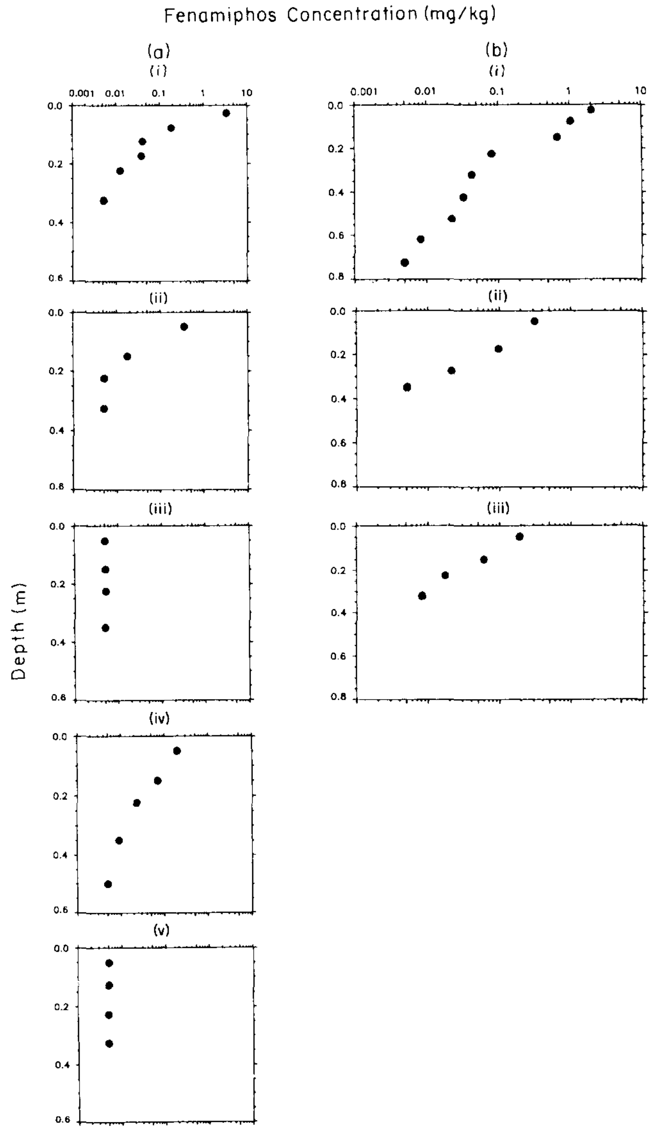

Fig. 6. Observed fenamiphos concentration profiles (note changes in axis scales). (a) Waiawa site at five times: (i) 4 days after first application; (ii) 38 days after first application; (iii) 124 days after first application; (iv) 213 days after first application, 17 days after second application; (v) 318 days after first application, 122 days after second application. (b) Poamoho site at three times: (i) 11 days after application; (ii) 53 days after application; (iii) 100 days after application. Note: fenamiphos reported as total fenamiphos which includes the parent compound and its metabolites fenamiphos sulfoxide and fenamiphos sulfone.

Soil-Water Content, Bulk Density, Soil Organic Carbon, and Hydrodynamic Dispersion Coefficient

Table 4 lists the measured and estimated soil-water content at field capacity, bulk density, soil organic carbon, and hydrodynamic dispersion coefficient profiles from the two test plots. Figure 7 summarizes the soil organic carbon contents from the transects (also see Loague, 1994; Yost et al., 1993); the complete listing of organic carbon data is reported by Miyahira (1990). Soils from the Poamoho test plot had a slightly lower surface f_{OC} value (0.017 kg/kg) than the Waiawa soil transect on Waiawa Ridge (0.025 kg/kg),

Table 2. Summary of Laboratory Pesticide Transformation Data

Site	Soil series	Depth (m)	Transformation rate (k) Chlorpyrifos (day^{-1})	r^2	Fenamiphos (day^{-1})	r^2
Waiawa plots	Kawaihapai	0.0 -0.10	0.083	0.905	0.187[1]	0.778
		0.2 -0.30	0.067	0.468	0.086[1]	0.624
Poamoho plots	Wahiawa	0.05-0.20	0.091	0.710	0.025	0.740
		0.35-0.55	0.103	0.478	0.031	0.936
Waiawa Ridge	Lahaina	0.05-0.20	0.064	0.903	0.030	0.790
		0.70-0.85	0.099	0.983	0.037	0.926
Waiawa Ridge	Molokai	0.05-0.25	0.065	0.951	0.026	0.822
		0.75-0.90	0.098	0.953	0.029	0.925
Waiawa Ridge	Wahiawa	0.05-0.20	0.051	0.947	0.024	0.666
		0.65-0.80	0.102	0.951	0.027	0.770

Note: Transformation rate coefficients were calculated from the first-order kinetics. The r^2 values (coefficient of determination from least-squares linear regression) describe the degree of fit to the linear form of the first-order equation.
[1]Transformation rate coefficient for fenamiphos (parent).

just as surface soils from the Waiawa test plot had a lower f_{oc} value (0.040 kg/kg) than the Kawaihapai transect within Waiawa Valley (0.054 kg/kg). No lateral spatial structure was observed along any of the transects, and f_{oc} was quite uniform along the Waiawa Ridge transects. Surface soils of the Kawaihapai series in Waiawa Valley had higher f_{oc} values, but nearly all of the sampled profiles were under 0.01 kg/kg below a depth of 0.5 m.

Discussion

The results from the laboratory and field experiments reported here lend themselves to a few generalized comments:

1. Bromide mass balance was good.
2. Both chlorpyrifos and fenamiphos exhibited only limited mobility to depths greater than 0.5 m at both exper-

Table 3. Summary of Laboratory Pesticide Sorption Data

Site	Soil series	Depth	Sorption coefficient (K_{oc}) Chlorpyrifos (m^3/kg)	r^2	Fenamiphos sulfoxide (m^3/kg)	r^2
Waiawa field site	Kawaihapai	Surface	1.18	0.988	0.043	0.989
	Kawaihapai	Subsoil	1.51	0.975	0.476	0.977
Poamoho field site	Wahiawa	Surface	1.67	0.997	0.054	0.990
	Wahiawa	Subsoil	1.27	0.988	0.088	0.956
Waiawa Ridge	Lahaina	—	1.22	0.958	0.493	0.806
	Molokai	—	1.27	0.967	0.375	0.982
	Wahiawa	—	1.41	0.981	0.496	0.807

r^2 = coefficient of determination, from the linear regression of sorbed versus solution concentrations for each soil. The slope of the regression line (Kd) was used to calculate K_{oc} using the relationship $K_{oc} = Kd/f_{oc}$.

Table 4. Soil and Hydrologic Parameters for the Waiawa and Poamoho Field Sites

Depth (m)	Soil-water content at field capacity[1], θ_{FC} (m^3/m^3)	Bulk density[1], ρ_b (kg/m^3)	Mass fraction of soil organic carbon[1], f_{oc} (kg/kg)	Hydrodynamic dispersion coefficients[2], D (m^2/day)
Waiawa				
0.0 -0.05	0.45	1100	0.040	0.002
0.05-0.1	0.45	1100	0.015	0.002
0.1 -0.2	0.45	1200	0.005	0.002
0.2 -0.3	0.45	1200	0.004	0.002
0.3 -0.5	0.50	1250	0.004	0.002
0.5 -0.6	0.50	1250	0.003	0.002
0.6 -0.8	0.50	1300	0.003	0.002
0.8 -1.0	0.50	1350	0.003	0.002
1.0 -3.0	0.50	1350	0.001	0.002
Poamoho				
0.0 -0.1	0.35	950	0.017	0.001
0.1 -0.2	0.37	1050	0.015	0.001
0.2 -0.3	0.37	1150	0.010	0.001
0.3 -0.4	0.40	1200	0.010	0.001
0.4 -0.5	0.40	1200	0.008	0.001
0.5 -0.7	0.40	1250	0.008	0.001
0.7 -2.5	0.42	1300	0.005	0.001

[1]Measured.
[2]Estimated.

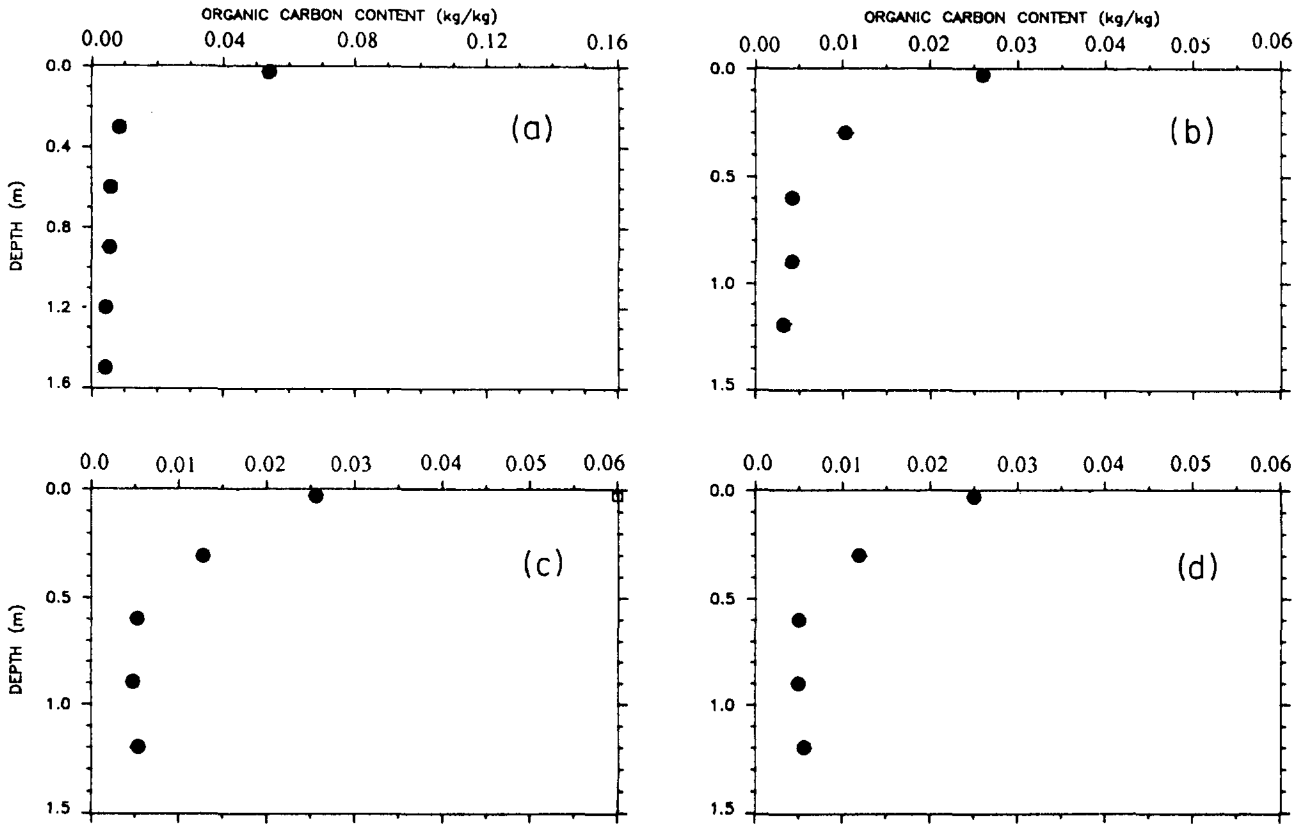

Fig. 7. Summary of average organic carbon profiles of four soils at Waiawa development sites (Miyahira, 1990). (a) Kawaihapai. (b) Lahaina. (c) Molokai. (d) Wahiawa.

imental sites, and were rapidly degraded, especially at the Waiawa site.

3. Variability in chemical movement between replicate plots was sufficient to be an important consideration for model evaluations, where experimental results are often considered to represent real-world truth. The coefficients of variation between test plots for chlorpyrifos and fenamiphos, based upon averaging the data for both field tests, were 0.41 and 0.33, respectively.

4. Soil organic carbon varied in space, both laterally in transects and with depth, to about the same extent for the four soil series. Differences greater than twofold for a single sampling network could have a significant effect on pesticide movement at different locations in the same development area. Coefficients of variation were calculated for the soil organic carbon data: for the Molakai, Lahaina, and Wahiawa soil series on the Waiawa Ridge the surface (0.03 m) and subsoil (0.3-1.2 m) values are 0.27 and 0.42, respectively; for the Kawaihapai soil series in the Waiawa Valley, the surface and subsoil values are 0.50 and 0.82, respectively.

Conclusions

The two field experiments which were established to assess chemical leaching provided a data base for the preliminary evaluation of our near-surface modeling effort (Loague et al., 1994). The utility of the type of experiments described here for determining long-term, deep leaching is limited due to scale restrictions in both time and space. The distribution of soil organic carbon collected along four transects did not show any obvious spatial structure.

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